DETERMINATION OF THE WAVE FUNCTION CORRESPONDING TO A REMOVED ELECTRON

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Using the methods of second quantization a formula for determining the wave function of an electron removed from an n-electron system can be derived by variation method.

Let us consider a k-electron system with the Hamiltonian

$$H^{(k)} = \sum_{i=1}^{k} h(x_i) + \frac{1}{2} \sum_{i,j}{}' v(x_i, x_j) \tag{1}$$

where x is an abbreviated notation for the space and spin variables. Let $\Phi^{(n)}(x_1, \ldots, x_n)$ be the wave function of the n-electron system in ground state:

$$H^{(n)} \Phi^{(n)} = E_0^{(n)} \Phi^{(n)}. \tag{2}$$

Operator $a_{n-1,n}[\chi]$ defined by

$$a_{n-1,n}[\chi] \Phi^{(n)} = \sqrt{n} \int dx_n \chi^*(x_n) \Phi^{(n)}_{(x_1, \ldots, x_{n-1}, x_n)} \equiv \Phi^{(n-1)}_{(x_1, \ldots, x_{n-1})} \tag{3}$$

is usually interpreted [1] as an operator removing an electron with the square integrable wave function $\chi(x)$ from the n-electron system described by the wave function $\Phi^{(n)}(x_1, \ldots, x_n)$.

The problem is to find the function $\chi_0(x)$ such that the function $\Phi^{(n-1)}$ defined by Eq. (3) be the best possible approximation of the ground state of the $n-1$-electron system.

Let us introduce the functional

$$E[\chi] = \frac{(\Phi^{(n-1)}, H^{(n-1)} \Phi^{(n-1)})}{(\Phi^{(n-1)}, \Phi^{(n-1)})}. \tag{4}$$

According to the variation principle, the best approximation of ground state energy $E_o^{(n-1)}$ of the $n-1$ electron system which can be found by varying the function $\chi(x)$ is just the minimum value of the functional $E[\chi]$. In this way Eq. (4) can serve to determine the function $\chi_0(x)$ by variation method.

We can write Eq. (4) in a simpler form. Let $\boldsymbol{\Phi}$ denote an element of the Fock-space [1], and let us assume that except its n^{th} component $\Phi^{(n)}(x_1, \ldots, x_n)$ all the other components vanish. Introducing the operators in the Fock space [1] $\mathbf{a}[\chi]$,

$\psi(x)$ and $\psi^*(x)$, supposing that the operator $v(x, y)=v(y, x)$ is independent of the momentum operator, one can find:

$$E[\chi]-E_0^{(n)} = -\frac{\int dx\, dy\, \chi^*(y)\left[h(y)\mu(y; x)+\int dz\, v(y, z)\sigma(z, y; z, x)\right]\chi(x)}{\int dx\, dy\, \chi^*(y)\mu(y; x)\chi(x)} \tag{5}$$

where μ and σ are tehe first-and second-order density matrices, respectively, [2, 3]:

$$\mu(y; y') = (\Phi, \Psi^+(y')\Psi(y)\Phi) = n\int dx_1 \ldots dx_{n-1}\Phi^{(n)*}_{(x_1, \ldots, x_{n-1}, y')}\Phi^{(n)}_{(x_1, \ldots, x_{n-1}, y)},$$

$$\sigma(z, y; z', y') = \left(\Phi, \Psi^+(y')\Psi^+(z')\Psi(z)\Psi(y)\Phi\right) =$$

$$= n(n-1)\int dx_1 \ldots dx_{n-2}\,\Phi^{(n)*}_{(x_1, \ldots, x_{n-2}, z', y')}\,\Phi^{(n)}_{(x_1, \ldots, x_{n-2}, z, y)}.$$

In the particular case of function $\Phi^{(n)}$

$$\Phi^{(n)}_{(x_1, \ldots, x_n)} = \sqrt{n!}\, A_n\{\varphi_1(x_1) \ldots \varphi_n(x_n)\} \tag{6}$$

where A_n denotes the antisymmetrizer

$$\mu(y; y') = \sum_{i=1}^{n}\varphi_i(y)\varphi_i^*(y'),$$

$$\sigma(z, y; z', y') = \mu(z; z')\mu(y; y') - \mu(z; y')\mu(y; z').$$

are obtained [3]. Function (6) can be used as approximate ground state wave function of the n-electron system if the functions $\varphi_i(x)$ $(i=1, 2, \ldots, n)$ are the Hartree-Fock orbitals:

$$\left\{h(y)+\sum_{j=1}^{n}\int dz\, \varphi_j^*(z)v(z, y)\,[1-P_{ij}]\varphi_j(z)\right\}\varphi_i(y) = \varepsilon_i\varphi_i(y)$$

where $P_{ij}\varphi_j(z)\varphi_i(y)=\varphi_i(z)\varphi_j(y)$. In this approximation

$$E[\chi] = E_0^{(n)} - \frac{\sum_{i=1}^{n}|\lambda_i|^2\varepsilon_i}{\sum_{i=1}^{n}|\lambda_i|^2}, \quad \lambda_i \equiv \int dx\, \varphi_i^*(x)\chi(x),$$

i. e. the minimum of $E[\chi]$ obtained by varying the function $\chi(x)$ is given by $E_0^{(n)}-\varepsilon_n$, where it is supposed that $\varepsilon_n = \max \varepsilon_i$. The corresponding function is: $\chi_0(x)=\varphi_n(x)$ According to (3), the ground state wave function of the $n-1$ electron system in this approximation is:

$$\Phi^{(n-1)}_{(x_1, \ldots, x_{n-1})} = \sqrt{(n-1)!}\, A_{n-1}\{\varphi_1(x_1) \ldots \varphi_{n-1}(x_{n-1})\}$$

In this case value $E[\chi_0]-E_0^{(n)}$ is connected with the ionization energy [4] and the same can be expected in the general case, too.

It is known, that the natural spin orbitals of a function of the type (6) are just the functions $\varphi_i(x)$, thus in such cases the function $\chi_0(x)$ determined from (5) is one of the natural spin orbitals; in this way $\chi_0(x)$ can be expected in general to be an approximation of a natural spin orbital. Numerical calculations for Li and Be^+, with the aim of supporting these conclusions, are in course.

References

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ОПРЕДЕЛЕНИЕ ВОЛНОВОЙ ФУНКЦИИ УНИЧТОЖЕННОГО ЭЛЕКТРОНА

И. К. Дьемант

Применением метода второй квантизации описывается формула, с помощью которой вычисляется волновая функсия электрона, уничтоженного из системы электронов.